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Studies on Sulfenamides. X.[1] Electron Spin Resonance Spectra of Radical Cations Electrochemically Generated from *N*-(*o*-Nitrophenylthio)alicyclic Amines

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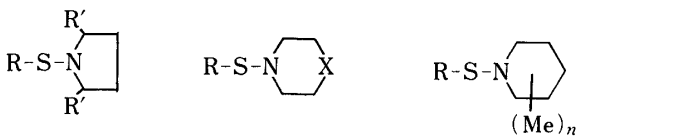
The paramagnetic species formed by *in situ* electrochemical oxidation of eleven *N*-(*o*-nitrophenylthio)alicyclic amines in acetonitrile or propionitrile have been identified as the radical cations derived from the parent sulfenamides by one-electron transfer. The observed non-equivalence of the two *N*-methylene groups indicated the existence of restricted rotation around the S–N bond and three-electron π-bonded geometry. As regards the radical cations derived from six-membered alicyclic sulfenamides, the ring inversion was apparently conformationally frozen on the electron spin resonance (ESR) time scale even at 25 °C. Based on the ESR and nuclear magnetic resonance data it is proposed that the C_2N–S group in these radical cations is pyramidal and that the nitrogen inversion of these radicals is slow on the ESR time scale. The stability of the radical cations is discussed.

Keywords——ESR; cation radical; sulfenamide; anodic oxidation; *in situ* electrolysis; N–S rotational barrier; sulfenamide radical cation; trialkylsulfenamide; electrochemical generation

In the previous papers,[1,2] we reported cyclic voltammetry and anodic oxidation of four *o*-nitrobenzenesulfenamide derived from secondary cyclic amines (pyrrolidine, thiomorpholine (tetrahydro-4*H*-1,4-thiazine), morpholine, and piperidine). The first step in the anodic oxidation of the sufenamides in acetonitrile was shown to be a quasi-reversible one-electron transfer to form the sulfenamide radical cations. The formation of the radical cations was confirmed by electron spin resonance (ESR) spectroscopy.

Although ESR spectra of *N*-thioaminyl radicals have been studied extensively by many workers,[3] only two papers have so far appeared on the ESR spectra of trialkylsulfenamide radical cations. Izuoka and Kobayashi[4] oxidized *N*,*N*-dimethyl- and *N*,*N*-diethylmethanesulfenamide by the use of aluminium chloride or titanium chloride in nitromethane to form radical cations. They tentatively proposed the two-center three-electron structure with a



1: R′=H
2: R′=Me

3: X=S
4: X=O

5: unsubstituted
6: 2-Me
7: 3-Me
8: 4-Me
9: 2,6-di-Me
10: 3,5-di-Me
11: 2,2,6,6-tetra-Me

R = *o*-nitrophenyl
Me = methyl

Chart 1

pyramidal C_2N–S group. Nelsen *et al.*[5] oxidized 1-(methylthio)pyrrolidine and 9-(methylthio)-9-azabicyclo(3,3,1)nonane by the use of tris(*p*-bromophenyl)aminium hexachloroantiminate in methylene chloride. They also proposed the three-electron π-bonded geometry but suggested a planar C_2N–S group. However, no definite evidence concerning the conformation of the C_2N–S group is available.

In the present paper we describe a detailed ESR study on the radical cations of *N*-(*o*-nitrophenylthio)alicyclic amines (**1**—**11**) at various temperatures. The radical cations were generated by *in situ* electrochemical oxidation at a platinum anode in acetonitrile or propionitrile.

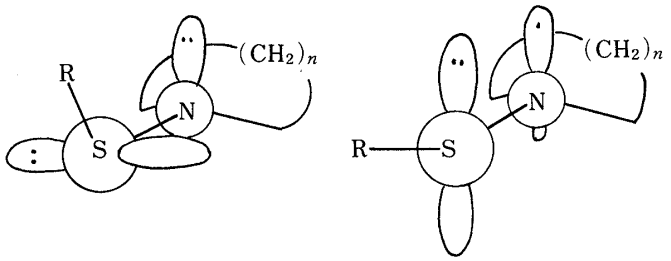
Results and Discussion

The ESR parameters required to match the experimental spectra by computer simulation are summarized in Table I. When the electrolytic current was turned off, the ESR signal intensity decayed with first-order kinetics. The apparent first-order rate constants obtained are also listed in Table I. Non-equivalence of the two *N*-methylene groups was observed for all radical cations. Although restricted rotation around the S–N bond of trialkylsulfenamides is well known,[6] the proposed conformation of the sulfenamides is one in which the nitrogen lone pair and the sulfur π-lone-pair axes are perpendicular to each other and the *o*-nitrophenyl ring lies within the plane containing the N–S bond and the nitrogen lone-pair orbital (A in Chart 2). Therefore, the parent sulfenamides possess a plane of symmetry, and the two *N*-methylene groups are equivalent, as confirmed by the proton magnetic resonance spectra (^{1}H-NMR) of the compounds. On the other hand, the proposed conformation of sulfenamide radical cations has the sulfur *p* orbital overlapping with the non-bonding orbital of the nitrogen sp^3 or *p* orbital to form the three-electron π-bonded geometry (B in Chart 2).[4,5] Thus, the radical cations studied here have no plane of symmetry. The observation of two different methylene-proton splittings indicates that the N–S rotational barrier is high on the ESR time scale.

TABLE I. ESR Parameters of the Cation Radicals Electrochemically Generated from *N*-(*o*-Nitrophenylthio)alicyclic Amines[a]

Parent compound	T (°C)	*g*-Value	Hyperfine coupling constants (G)[e]	k_{obs}[b] (min^{-1})
1	25	2.0061	14.3 (N), 20.0 (2H), 19.0 (2H)	9.9
1	−90[c]	2.0061	14.0 (N), 21.5 (1H), 20.3 (1H), 19.7 (1H), 14.7 (1H)	
2	25	2.0062	13.6 (N), 21.5 (1H), 14.8 (1H)[f]	49
3	25	2.0061	13.7 (N), 19.7 (1H), 13.4 (1H)	41
3	−40	2.0062	13.1 (N), 20.5 (1H), 13.5 (1H)	
4	25	2.0061	14.2 (N), 21.6 (1H), 15.2 (1H)	11
4	−40	2.0061	13.4 (N), 21.7 (1H), 14.6 (1H), 2.8 (1H), 1.3 (1H)	
5	−30	2.0060	14.0 (N), 22.7 (1H), 16.1 (1H), 1.8 (1H), 0.95 (8H)	3.3
6	25	2.0060	Not assigned	4.1
7	25	2.0061	14.3 (N), 22.1 (1H), 16.4 (1H)	2.6
8	25	2.0061	14.0 (N), 22.5 (1H), 17.3 (1H), 1.8 (1H), 0.95 (7H)	3.4
9	−30	2.0062	A [14.6 (N), 5.5 (1H), 2.7 (1H)]; B [14.6 (N), 2.4 (1H), 1.9 (1H)][d]	26
10	25	2.0061	14.1 (N), 21.9 (1H), 16.6 (1H)	2.9
11	25	2.0067	12.7 (N), 2.0 (2H), 1.0 (3H)	4.2

a) The radical cations were generated in acetonitrile unless otherwise noted. *b*) First-order rate constant for the decomposition of the radical cations in acetonitrile at 25 °C. *c*) In propionitrile. *d*) A mixture of two radicals, A/B = 3. *e*) Estimated error, ±0.1 G unless otherwise stated. *f*) Estimated error, ±0.2 G.



sulfenamide (A) radical cation (B)

Chart 2

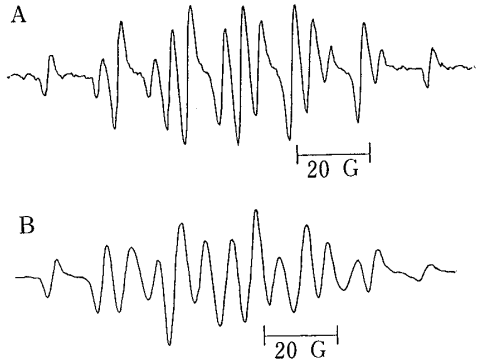


Fig. 1. ESR Spectra of an *in Situ* Electrolyzed Solution of **1** in Acetonitrile at 25 °C (A) and in Propionitrile at −90 °C (B)

In all spectra the magnetic field increases from left to right. Instrumental settings: power, 1 mW; modulation amplitude, A 1.6 G, B 0.2 G; scan rate, 50 G/min; gain, A 2×1000, B 5×100.

N-(*o*-Nitrophenylthio)pyrrolidine Radical Cation ($1^{+}\cdot$)

In situ electrolysis of **1** in propionitrile at −90 °C gave an ESR spectrum different from that obtained at 25 °C, as shown in Fig. 1. In the previous paper,[1] it was proposed that the axial and equatorial protons interchange rapidly. On the other hand, the spectrum at −90 °C showed splittings arising from four different β-protons, which indicates that the radical cation is apparently frozen in one conformation on the ESR time scale.

N-(*o*-Nitrophenylthio)-2,5-dimethylpyrrolidine Radical Cation ($2^{+}\cdot$)

Electrolysis of **2** in acetonitrile at 25 °C gave an ill-defined 8-line ESR spectrum, though approximate hyperfine coupling constants (*hfsc*'s) were recognizable. The radical cation from **2** was the most unstable among the compounds studied. Electrolysis of **2** at lower temperatures gave a very complex ESR spectrum, and we could not simulate the spectrum. This is not unexpected, because **2** is a mixture of *cis* and *trans* forms, and the observed spectrum derives from a mixture of several conformations of two isomers.

N-(*o*-Nitrophenylthio)thiomorpholine Radical Cation ($3^{+}\cdot$)

Electrolysis of **3** in acetonitrile at −40 °C gave a well-defined 8-line spectrum similar to that obtained at 25 °C. There were large coupling constants due to only two of the possible four β-protons. These results indicate that the radical cation derived from **3** is apparently conformationally frozen on the ESR time scale event at 25 °C. This would be expected if the six-membered heterocyclic ring existed in a chair conformation. This would allow one proton on each α-carbon atom to be in the axial position, for which a large coupling constant would be expected, and the remaining β-proton would be equatorial and would be expected to show a small coupling constant which could not be resolved in the observed spectra.[7]

N-(*o*-Nitrophenylthio)morpholine Radical Cation ($4^{+}\cdot$)

Electrolysis of **4** in acetonitrile at −40 °C showed an 8-line spectrum in which each peak was partially split to two peaks by small proton couplings. Retention of an 8-line pattern at −40 °C suggests that ring inversion of $4^{+}\cdot$ is conformationally frozen on the ESR time scale

at 25 °C, and hence the variation of the spectrum at low temperatures may be ascribed to another factor, as will be discussed further in the next section.

N-(*o*-Nitrophenylthio)piperidine Radical Cation ($5^+\cdot$)

Electrolysis of **5** at 25 °C gave an ill-defined spectrum, as shown in Fig. 2. The spectrum could not be simulated as being derived from a single radical species. Electrolysis of **5** at −30 °C gave a well-defined spectrum as shown in Fig. 2. Each peak of the 8-line pattern was partially resolved by small splittings with one proton and eight equivalent protons. Since the spectrum at 25 °C retained an 8-line pattern which is similar to that of $3^+\cdot$, both ring inversion and rotation around the S–N bond in $5^+\cdot$ are considered to be frozen even at 25 °C. Therefore, the difference between the spectra of $5^+\cdot$ at 25 °C and −30 °C must be attributed to other conformational changes. Although the conformation of the C_2N–S group in the sulfenamide radical cations has not been established, we propose here a pyramidal conformation. That is, two conformations with the *o*-nitrophenylthio group occupying an equatorial position and an axial position at the nitrogen would be present, and the two conformations would be interchanging slowly on the ESR time scale at 25 °C, whereas at −30 °C $5^+\cdot$ becomes frozen in one preferred conformation. This assumption was substantiated by analysis of the carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectrum of **9**. Since 2,6-dimethylpiperidine used for synthesizing **9** was in *cis* form as confirmed by ^{13}C-NMR, **9** obtained should contain only the *cis* isomer. However, the ^{13}C-NMR spectrum of **9** in $CDCl_3$ at 25 °C showed the presence of two isomers; δ: 19.3 (s, CH_3), 21.3 (s, CH_3), 24.1 (s, C(4)), 25.1 (s, C(4)), 31.2 (s, C(3, 5)), 36.4 (s, C(3, 5)), 60. 3 (s, C(2. 6)), 60.6 (s, C(2, 6)), and aromatic carbons. Differences in the chemical shifts of the two methyl peaks and the two C(4) peaks were too small to represent those expected between axial and equatorial positions. On the other hand, the difference in chemical shift of the two C(3, 5) peaks was fairly large. These results suggest that two conformations with the *o*-nitrophenylthio group occupying an equatorial position and an axial position exist in **9** on the NMR time scale at 25 °C. Since the NMR time scale is much longer than the ESR time scale, the presence of the two conformers in $5^+\cdot$ at 25 °C is not unreasonable.

Although unambiguous assignment of the small *hfsc*'s in the spectrum at −30 °C is difficult from the present data, the total number of protons which give *hfsc*'s is eleven and

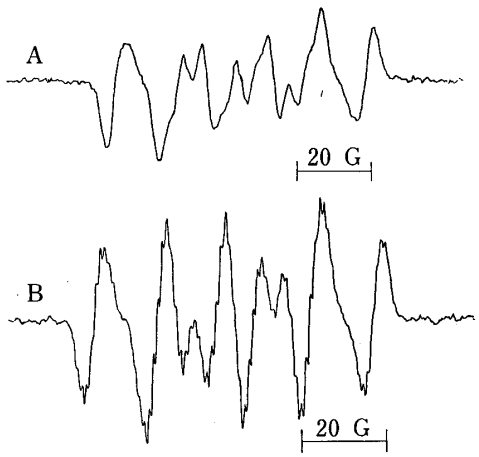


Fig. 2. ESR Spectra of an *in Situ* Electrolyzed Solution of **5** at 25 °C (A) and −30 °C (B) in Acetonitrile

Instrumental settings: power, 1 mW; modulation amplitude, A 1.0 G, B 0.16 G; scan rate, 50 G/min; gain, A 2 × 1000, B 1.6 × 1000.

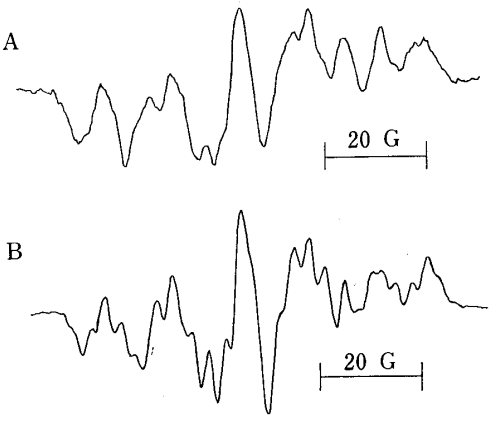


Fig. 3. ESR Spectra of an *in Situ* Electrolyzed Solution of **6** at 25 °C (A) and −30 °C (B) in Acetonitrile

Instrumental settings: power, A 5 mW, B 1 mW; modulation amplitude, A 2.0 G, B 0.63 G; scan rate, A 50 G/min, B 25 G/min; gain, 1.25 × 1000.

hence the protons in the *o*-nitrophenyl group must participate in the *hfsc*'s. Since the values of *hfsc*'s of the protons at the 4 and 6 positions in *o*-nitrobenzenesulfenanilidyl radicals are about 0.8 G,[8] the above deduction is not unreasonable.

N-(*o*-Nitrophenylthio)-2-methylpiperidine Radical Cation ($6^{+}\cdot$)

Electrolysis of **6** at 25 °C gave a complicated spectrum which could not be simulated as being derived from a single radical species. At −30 °C the spectrum showed additional small splittings as shown in Fig. 3. The ^{13}C-NMR spectrum of **6**, in which the protons attached to the piperidine ring showed broad peaks, suggests that the rate of interconversion is intermediate and that the preferred conformation of the methyl group is equatorial. Since 2-methylpiperidine does not have a plane of symmetry, additional conformations in terms of the orientation of the *o*-nitrophenyl group exist as shown in Chart 3, and these are considered to be responsible for the complicated spectrum.

N-(*o*-Nitrophenylthio)-3-methylpiperidine Radical Cation ($7^{+}\cdot$)

Electrolysis of **7** at 25 °C gave a well-defined 8-line spectrum. The 8-line pattern was unchanged at lower temperatures. Although additional conformations similar to those of $\mathbf{6}^{+}\cdot$ are expected for $\mathbf{7}^{+}\cdot$, the position of methyl substitution is at carbon β to nitrogen, and hence the conformational difference is assumed to have little effect on the β-proton *hfsc*'s.

N(*o*-Nitrophenylthio)-4-methylpiperidine Radical Cation ($8^{+}\cdot$)

Electrolysis of **8** at 25 °C gave a well-defined 8-line spectrum as shown in Fig. 4. Each peak of the spectrum was partially resolved further by additional small splittings. These splittings became evident at 0 °C. The ESR parameters of $\mathbf{8}^{+}\cdot$ were similar in magnitude to those of $\mathbf{5}^{+}\cdot$, but the number of equivalent protons with the smallest *hfsc* decreased from eight to seven. Since the ^{13}C-NMR spectrum of **8** showed a strong conformational preference for an equatorial methyl group, one of eight equivalent protons of $\mathbf{5}^{+}\cdot$ can be assigned to an equatorial proton at the 4-position. Similar equatorial δ proton *hfsc*'s have been reported for 4-alkylpiperidine nitroxides.[9] The protons in the *o*-nitrophenyl group must participate in the *hfsc*'s in the same manner as in $\mathbf{5}^{+}\cdot$. The observation of the small splittings for $\mathbf{8}^{+}\cdot$ at 25 °C suggests that the introduction of a methyl group at the 4-position brings about an increase in the population of the preferred conformation.

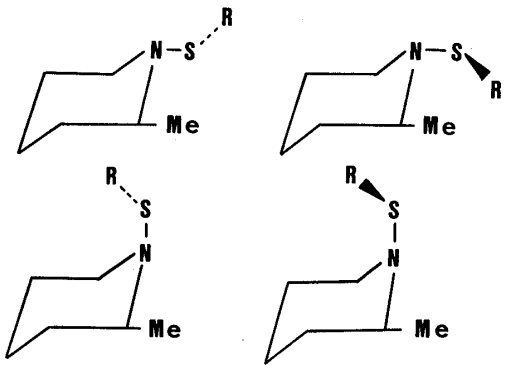


Chart 3

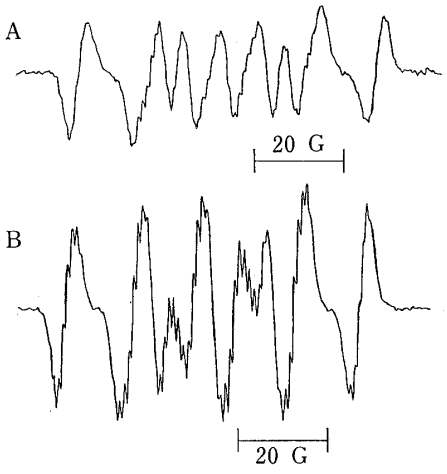


Fig. 4. ESR Spectra of an *in Situ* Electrolyzed Solution of **8** at 25 °C (A) and 0 °C (B) in Acetonitrile

Instrumental settings: power, A 5 mW, B 1 mW; modulation amplitude, A 0.63 G, B 0.2 G; scan rate, 50 G/min; gain, A 1.6 × 1000, B 1 × 1000.

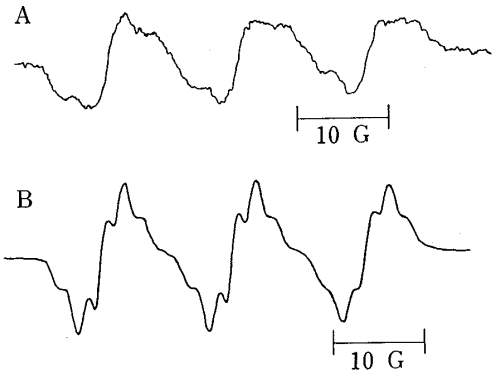


Fig. 5. ESR Spectra of an *in Situ* Electrolyzed Solution of **9** at 25 °C (A) and −30 °C (B) in Acetonitrile

Instrumental settings: power, A 5 mW, B 0.2 mW; modulation amplitude, A 2.0 G, B 0.32 G; scan rate, 25 G/min; gain, A 2 × 1000, B 3.2 × 100.

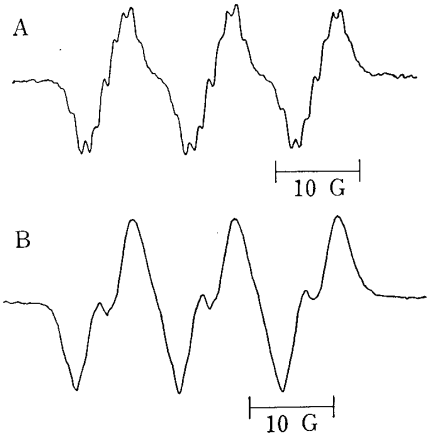


Fig. 6. ESR Spectra of an *in Situ* Electrolyzed Solution of **11** at 25 °C (A) and −30 °C (B) in Acetonitrile

Instrumental settings: power, A 5 mW, B 0.2 mW; modulation amplitude, A 0.25 G, B 0.2 G; scan rate, 25 G/min; gain, A 1.6 × 1000, B 6.3 × 100.

N-(*o*-Nitrophenylthio)-2,6-dimethylpiperidine Radical Cation ($9^{+}\cdot$)

Electrolysis of **9** at 25 °C gave an ill-defined spectrum, from which only the nitrogen *hfsc* was obtained ($A_N = 14.3$ G). On electrolysis of **9** at −30 °C a fairly well-defined spectrum was obtained as shown in Fig. 5. However, the spectrum could not be simulated as being derived from a single radical species. As described in the previous section, **9** exists in two frozen conformations with the *o*-nitrophenylthio group occupying an equatorial position and an axial position, and hence $9^{+}\cdot$ is also considered to be frozen in two conformations. The absence of large proton *hfsc*'s suggests that both methyl groups in $9^{+}\cdot$ occupy axial positions, unlike the methyl groups in **9**. This is consistent with the three-electron π-bonded geometry B of $9^{+}\cdot$ in Chart 1, which favors the di-axial conformation rather than the di-equatorial one.

N-(*o*-Nitrophenylthio)-3,5-dimethylpiperidine Radical Cation ($10^{+}\cdot$)

Electrolysis of **10** at 25 °C gave a fairly well-defined 8-line spectrum, which closely resembles the spectrum of $7^{+}\cdot$. The 8-line pattern was unchanged at lower temperatures. Although **10** is a mixture of *cis* and *trans* isomers as confirmed by ^{13}C-NMR (Table II), the positions of methyl substitution are at carbon β to nitrogen, and hence the conformational difference is assumed to have little effect on β-proton *hfsc*'s as in the case of $7^{+}\cdot$.

N-(*o*-Nitrophenylthio)-2,2,6,6-tetramethylpiperidine Radical Cation ($11^{+}\cdot$)

Electrolysis of **11** at 25 °C gave a well-defined spectrum with a nitrogen *hfsc* and small proton *hfsc*'s as shown in Fig. 6. As the temperature was lowered, the spectrum gradually broadened and showed couplings only from one nitrogen (12.4 G) and one proton (2.8 G) at −40 °C. Since **11** exists in a single frozen conformation at 25 °C as determined by ^{13}C-NMR and the tetramethylpiperidine ring has a plane of symmetry, $11^{+}\cdot$ is also considered to exist in a single conformation at 25 °C, and the small *hfsc*'s were observed even at 25 °C. The broadening of the spectrum at lower temperatures can be ascribed to a decreased rate of rotation of the methyl groups. The smallest nitrogen *hfsc* and the largest *g*-value of $11^{+}\cdot$ among the radical cations studied suggest that the conformation of the C_2N–S group in $11^{+}\cdot$ is somewhat different from those in the other sulfenamide radical cations because of steric interaction between the methyl groups.

Stabilities of the Radical Cations

Inspection of the first-order rate constants for the decomposition of the radical cations

suggests that at least two pathways are present for the decomposition. One is a nucleophilic attack on the sulfur nucleus leading to formation of a sulfenylium ion and an aminyl radical.[1] Since divalent sulfur is a strong soft-base,[10] the nucelophilic attack of **3** on $\mathbf{3}^{+}\cdot$ is the most powerful among the compounds studied, and hence $\mathbf{3}^{+}\cdot$ has the shortest life-time among the sulfenamides with a six-membered ring. This was confirmed by cyclic voltammetry; that is, the cathodic counterpart of the first anodic peak of **4** (2 mM) completely disappeared on addition of 6 mM pentamethylenesulfide.

Another pathway is deprotonation at carbon α to nitrogen followed by another one-electron oxidation.[1] Although substitution of protons at the 2 and 6 positions with two methyl groups greatly increased the decomposition rate, substitution of all four protons at the 2 and 6 positions only slightly increased the rate. Since $\mathbf{11}^{+}\cdot$ has no proton at carbon α to nitrogen, $\mathbf{11}^{+}\cdot$ should decompose exclusively through S–N bond fission. Detailed studies on this are in progress.

Experimental

Materials——*N*(-*o*-Nitrophenylthio)alicyclic amines were prepared as described previously.[2] Compounds **1**, **3**—**5** were purified as described previously,[2] and **2** was purified by chromatography on a pre-packed LiChroprep Si60 column (E. Merck, 440-37, size C, 40—60 μm) with benzene–hexane (1 : 1) as an eluent. Compounds **6**—**10** were purified by extraction with hot ethanol followed by chromatography on the same column as above with benzene–hexane (1 : 2) as an eluent, and **11** was purified by recrystallization from ethanol. Compounds **9** and **11** were yellow crystals, which had mp's of 70 and 90 °C, respectively. The strucures of **2** and **6**—**11** were confirmed by analysis of the ^{13}C-NMR spectra, as summarized in Table II.

Methods——ESR spectra were recorded on a JEOL JES-FE 1X spectrometer equipped with 100 kHz field modulation and a ES-UCT-2AX variable temperature accessory. The electrolysis cell used for internal generation of the radical cations was a Pyrex capillary (i.d., 1 mm; length, 100 mm) with a Pyrex reservoir (i.d., 10 mm; length 70 mm) at the top. The cell was attached to the ESR spectrometer so that the central region of the capillary was located in the center of the ESR cavity. A platinum wire anode, which was covered by polyethylene tubing except at both ends, was inserted into the capillary and a platinum wire cathode was placed in the reservoir. A solution of a sulfenamide (*ca.* 10 mM) in acetonitrile or propionitrile containing 0.1 M sodium perchlorate was deoxygenated in the reservoir by flushing with dry N_2 gas, and then introduced into the capillary. The solution was subjected to constant current electrolysis (0.01 mA), which was performed with a Hokuto-Denko HA-111 potentiostat-galvanostat, and the ESR spectrum was monitored. During the electrolysis, N_2 gas was passed over the solution. The *g*-value was

Table II. The Results of ^{13}C-NMR Spectroscopy of *N*-(*o*-Nitrophenylthio)-alicyclic Amines[a]

Compound	Chemical shift (δ; ppm) of alicyclic part[b]					
	C(2)	C(3)	C(4)	C(5)	C(6)	CH_3
2[c]	63.1	31.7	31.7	63.1	—	21.9
	59.8	32.5	32.5	59.8	—	20.2
	58.4	32.1	32.1	58.4	—	19.5
6	58.5	34.7	23.5	27.2	56.7	19.4
7	63.4	32.0	32.4	26.0	55.8	19.2
8	55.8	35.4	29.8	35.4	55.8	21.8
9[d]	60.6	31.2	25.1	31.2	60.6	19.3
	60.3	36.4	24.1	36.4	60.3	21.3
10[e]	62.9	31.0	41.3	31.0	62.9	19.1
	62.6	28.5	37.8	28.5	62.6	18.1
11	59.8	41.2	17.4	41.2	59.8	31.3, 25.2

a) $CDCl_3$ was used as a solvent. *b*) Unambiguous assignment of the signals of aromatic carbons was not made. *c*) Mixture of three conformers derived from two isomers. *d*) Mixture of two conformers (average ratio of integrals 1 : 0.56 (upper : lower)). *e*) Mixture of two isomers.

determined by comparing the spectrum with that of aqueous peroxylamine disulfonate ($g=2.0055$). Computer simulation of the spectrum was carried out using a JEOL EC-100 computer system.

Proton and ^{13}C-NMR spectra were recorded on a Bruker AM-400 spectrometer in $CDCl_3$ with tetramethylsilane as an internal standard, at 400 and 100 MHz, respectively.

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